# **Derivations for the Flash equation:**

**The derivation path that is matching our experimental work is: Nernst/Gibbs → add field work → subtract vibrational free energy via the universal phonon theory → Flash equation**

# Start from electrochemistry (Nernst → electrical work)

Consider a generic oxide reduction written per metal cation M with oxidation state ν:

The isothermal non-PV work that an applied electric field does on the charged species over a characteristic hop/escape distance ℓ is:

where is the charge number carried per mole of species (in Faradays). For oxygen removal, each carries . If we idealize the redox event as ejecting an across (on average) a distance (from a defect/nanodomain into the field-accelerated escape path), and we need oxyanions per metal reduced, then

For the common dioxides (ν=4, e.g., TiO₂), this reduces to

This exact factorization is the origin of the “” term we’ve been using is the electrical work available to do chemical work on the oxide (you can generalize it as for arbitrary valence ν). Through the Nernst relation, electrical work and chemical affinity are linked by (with overpotential ); here we’re writing the field-coupled contribution directly as an additive work term to the free energy landscape, hence the sign choice below.

# **Thermodynamics (Gibbs driving force)**

Let be the equilibrium Gibbs free energy change for the oxide reduction (the Ellingham value per mole M reduced). In a uniform axial field with characteristic escape radius , the field-modified free energy is

When , the reaction is driven “downhill” even at temperatures where in equilibrium.

# **We add the vibrational (phonon) softening correction**

The universal phonon theory shows that disorder- and resonance-induced damping softens the dispersion , produces an excess vibrational density of states (VDoS) (boson-peak/Van-Hove evolution), and thereby changes the vibrational free energy of a solid away from the Debye baseline. In compact form (harmonic lattice thermodynamics),

so any softening that adds low-ω weight (relative to the Debye model) lowers and thus the Gibbs free energy of the oxide (and/or the transition state for oxygen release). The Nature Physics model derives (i) a Green’s-function framework for the damped phonons, (ii) a q-dependent damping law that crosses from Rayleigh to quadratic (Mie-like) with resonance, and (iii) the resulting and heat-capacity anomalies that parameterize this softening across materials classes. (Nature Physics, Universal Phonon Theory, 2025).

Concretely (symbols as in that work):

* Damped phonon response and VDoS are obtained from the Green’s function, linking damping to softening and thence to an excess VDoS at low frequencies (boson-peak/VHS evolution).
* This excess low-ω VDoS yields a vibrational free-energy decrease relative to Debye: , which we use as a work-like contribution available to assist oxygen release (the “phonon pump” term).

A very useful high-T (classical) approximation expresses the vibrational free energy with an effective Debye temperature that encodes the softening (mathematically it reproduces the boson-peak systematics in that paper):

with when (softened lattice). This captures the *magnitude* of the phonon-assisted lowering without having to integrate the full every time; the unified model gives you the materials-dependent (or equivalently the boson-peak parameters) from , , , or .

# **The “Flash” driving equation**

Adding the electrical work and the phonon softening correction to the equilibrium Gibbs driver gives the current Flash equation:

with the practical approximation

(and for general valence : replace by ).

# **Definition of the plotting/decision metric “ΔB”**

For phase-diagramming and “how much easier it is to process under Flash” it’s helpful to work with a margin that’s positive when the process is downhill.

Define

so that

Interpretation:

* is the equilibrium margin (negative below the Ellingham crossover, positive above).
* is the field-work margin that shifts Ellingham lines down by a constant offset (per geometry and field ).
* is the phonon margin from softening (grows with the boson-peak intensity / depression at the relevant ).

**Flash is “on” when .**

## Quick recipe to compute two ways

1. Boson-peak (heat-capacity) route (fast): From data, fit the excess peak (height , position ) with the unified model; convert to an effective and use . The Nature Physics work shows how one set of parameters collapses many materials and links directly to peaks and VDoS softening.
2. VDoS (microscopic) route (accurate): Use the model’s (resonant Rayleigh→quadratic crossover) to get , then from the Green’s function; evaluate

where is the excess VDoS (softened minus Debye). The same paper lays out the needed equations and shows fits across 143 solids (crystals, HEAs, glasses), which is why we’re comfortable using this term as a general, materials-agnostic correction.

## **Variables:**

* : axial electric field (V m⁻¹)
* : characteristic escape radius for an (m)
* : Faraday constant (C mol⁻¹)
* : cation valence (dimensionless); TiO₂ →
* : Ellingham free energy per mole M reduced (J mol⁻¹)
* : Debye and effective Debye temperatures (K)
* : vibrational free-energy lowering due to softening (J mol⁻¹)
* : *margin* (positive = downhill under Flash), with units of J mol⁻¹ on the same basis as

## **There are 3 ways to put a part in a state of Flash: 1) current, 2) voltage, 3) field. The following equations outline how you do it with each mode:**

For modeling pick a sample shape: gauge length , cross-sectional area , resistivity conductivity

Then compute:

The volumetric power input is:

* Current-controlled (CC):
* Voltage/field-controlled (CV/EF):

Thermal balance: where represents total heat loss (conduction, radiation, etc.).

At steady-state :

Thermal runaway onset occurs when the input power’s temperature derivative equals that of the losses:

## **Critical current density (J\_crit, current-controlled entry mode)**

For current control:

Runaway condition gives:

Metals: → CC produces positive feedback → Flash possible.

Ceramics and Glasses: → CC is self-stabilizing → Flash not triggered by current control unless the part temperature is high enough to have enough ionic conductivity. In that case heat the part first or self heat via CV, then switch to CC.

## **Critical field (E\_crit, voltage-controlled mode)**

For voltage or field control:

Runaway condition:

**Ceramics:**  → is real → Flash achievable under EF/CV.

**Metals**: → imaginary → Flash not achievable in a solid by pure voltage control but it can be achieved if the starting material is a metal powder or compact. Metal powders / oxide-coated compacts / percolative systems → despite being “metallic” by composition, they often behave like insulators before necking; CV/EF can trigger the transition, after which the supply usually hits a current limit and stable Flash can be sustained in CC mode.

## **Mixed control (practical power supplies)**

Laboratory power supplies often have a series resistance . Effective regime depends on the ratio of to sample resistance :

* Metals: need nearly current control →
* Ceramics: need nearly voltage (field) control →

## **Transport models for**

### Metals: For metals above Θ\_D/3 (Bloch–Grüneisen regime):

* Near flash conditions, is the resistivity slope at the pre-flash temperature .

### Ceramics / semiconductors typical conduction laws:

* Arrhenius (band/polaron): Plug into expression.
* Small-polaron hopping:
* Poole–Frenkel (field-assisted):

Field lowers because the second term increases negative slope.

## Combined thermal + chemical criterion, Flash occurs when both conditions are met:

* Thermal criterion: (for metals) and (for ceramics)
* Chemical criterion:

You can adjust parameters to satisfy both: Increase (shorter sample or higher voltage), Decrease (smaller grain/domain), Raise (preheat or ramp rate), Enhance (phonon softening)

## Thermal loss coefficient Λ: Approximate total heat loss per unit volume as:

where:

* = thermal conductivity to clamps
* = conduction length
* = convective coefficient (if in gas)
* = emissivity
* = Stefan–Boltzmann constant

| Control Type | Driver | Runaway Condition | Flash Behavior |
| --- | --- | --- | --- |
| **Current (metals)** |  |  | Positive feedback (dρ/dT>0) |
| **Voltage (ceramics)** |  |  | Positive feedback (dρ/dT<0) |

Conversion:

Flash “onset” corresponds to:

## **Special cases:**

Metal (linear resistivity):

* Ceramic (Arrhenius):

## **Metal vs Ceramic Summary**

| **Property** | **Metals** | **Ceramics/Semiconductors** |
| --- | --- | --- |
| **dρ/dT** | Positive | Negative |
| **Dominant mode** | Current control (CC) | Field control (CV/EF) |
| **Flash onset variable** | J\_crit | E\_crit |
| **Typical trigger** | Resistive heating → phonon softening | Field-enhanced conduction |
| **W\_ph significance** | Near or above Debye temp | Even at lower T via defect incubation modes |
| **Flash condition** | ΔB > 0 at J ≥ J\_crit | ΔB > 0 at E ≥ E\_crit |